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High-precision stable isotope analysis of less than 5 microgram carbonate samples by continuous-flow mass spectrometry

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Stable isotope analysis of biogenic carbonates has remained one of the most important tools in paleoceanography since Emiliani (1955) first described the fluctuation of oxygen isotopes in planktic foraminifers over the Pleistocene. Many laboratories now possess equipment with the capability to analyse foraminifer specimens singularly, at least for larger planktic forms.

Being able to run single specimens of planktic foraminifers is significant, because it yields entirely different information than when one would analyse multiple specimens from the same species. Planktic foraminifers have an average life span of about one month, so analysing single specimens, makes paleoceanographic data at seasonal resolution available (e.g. Ganssen et al., 2011; Metcalfe et al 2019, and references therein).

Most modern equipment for stable isotope analysis of CaCO₃ samples yields good precision down to 10 microgram sample size. The smallest samples are generally measured with a dual inlet technique, because that quantitatively collects the CO₂ gas sample in a cold trap before analysis, leading to a more efficient use of the sample gas. Modern dual inlet equipment has a sample size limit somewhere between 10 and 6 microgram CaCO₃ sample weight, and in that range usually operates at increased analytical uncertainty when compared to larger samples (e.g. Ganssen et al., 2011). Smaller samples are problematic, because at small amounts of sample gas, the dual inlet system is not able to maintain viscous flow conditions required for precise isotope analysis. To circumvent that barrier, one can use continuous-flow (CF) mass spectrometry because in CF systems the carrier gas ensures proper flow conditions even if there is (virtually) no sample gas produced. Doing so has previously allowed for the isotope analysis of CaCO₃ samples in the 10 – 6 microgram range at an external precision (1SD) of ~0.12‰ for both δ¹⁸O and δ¹³C (e.g. Metcalfe et al 2019).

To further improve the performance of CF mass spectrometry for small CaCO₃ samples, we ran experiments on a Thermo GASBENCH system, equipped with a cold trap (cf. Fiebig et al 2005) and interfaced with a Delta-V mass spectrometer. The experiments consisted of replicate analysis of CaCO₃ standards between 10 and 3 micrograms in weight, which is the weight range of many of the smaller specimens of planktic foraminifers.

Several hardware modifications were implemented to improve system stability and remove observed effects of contribution of blank CO₂ building up in the sample vials. With these modifications, external reproducibility of the set-up for carbonate standard aliquots between 10 and 4 microgram reached a precision of ~0.10 ‰ for both δ¹⁸O and δ¹³C (1SD). This is similar to precisions typically attained for routine analysis of much larger samples in standard operation on the same equipment, and demonstrates that precise stable isotope analysis of smaller single-specimen planktic foraminifers than we could achieve so far is within reach of CF mass spectrometry.

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